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Study of Iron Oxidation in Sulfur Dioxide Atmospheres by Means of the ^{35}S Radioisotope

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Results of investigations of the mechanism of iron oxidation in atmosphere containing sulfur dioxide are presented. Experiments were carried out both by the platinum marker method and by means of the two-stage oxidation method using sulfur dioxide labeled with the ^{35}S radioisotope. SO_2 partial pressures applied were 0.03 and 1 atm at 800°C. The reaction occurred by outward diffusion of iron ions at both sulfur pressures. In addition to cation diffusion there was also some inward sulfur penetration which occurred, however, not by volume diffusion but by short-circuit paths. At the lower SO_2 partial pressure these paths are probably discontinuities in the scale (microfissures), whereas, for $p = 1$ atm, the inward penetration paths are probably large cavities produced by dissociation at the edges of the specimen when the reaction time is long enough.

KEY WORDS: mechanism of oxidation; two-stage oxidation method; marker method; autoradiographs; transport of reagents.

INTRODUCTION

It is generally accepted that in atmospheres containing SO_2 under partial pressures of sulfur and oxygen resulting from the value of the SO_2 dissociation constant there should be no formation of FeS. It has been found, however, that as a result of oxidation of iron in sulfur dioxide both iron oxide and the sulfide are formed. The morphological structure of the scale depends on the partial pressure of SO_2 in the gas and on the temperature of the reaction.[1,2,3,7]

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Several possible explanations of this fact have been proposed by Rahmel.[4] This author considers, among others, the possibility of inward penetration of the reacting gas into the scale through microfissures in the scale as well as inward volume diffusion of sulfur through the oxide.

The purpose of this paper is to investigate whether, during the scale growth process, inward diffusion of sulfur really occurs and, if so, what its mechanism is.

EXPERIMENTAL

A two-stage oxidation method has been used (the first stage of the reaction occurring in nonradioactive gas, the second in radioactive gas) with sulfur dioxide labeled by the radioisotope ^{35}S. The surface of the specimen was marked with thin platinum wires (0.08 mm diameter). The labeled SO_2 gas was obtained either by the reaction of anhydrous sodium sulfide (labeled with ^{35}S) with concentrated sulfuric acid or by the direct burning of labeled sulfur in oxygen.

The specimens used were ARMCO-iron disks 17 mm in diameter containing about 0.6% metallic and nonmetallic impurities. Before each measurement they were ground with 800 grade carborundum paper and degreased in acetone.

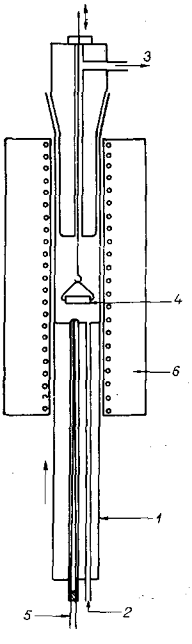

Fig. 1. Diagram of the apparatus. (1) Quartz tube; (2) gas inlet; (3) gas outlet; (4) specimen; (5) Pt/Pt–Rh thermocouple; (6) heated part of the furnace.

The oxidation was carried out in a quartz resistance furnace (Fig. 1) at 800 ± 10°C. The temperature was controlled by a Pt/Pt–Rh thermocouple connected to a recorder. The atmosphere was either gaseous SO_2 at 1 atm or an argon–sulfur dioxide mixture with an SO_2 partial pressure of 0.03 atm. In order to get rid of oxygen the argon gas was fed through a hot column containing copper turnings. Before arriving in the mixer each component of the gas mixture was dried over silica gel and fed through flow meters. After mixing, the gas mixture was fed into the furnace. In all runs the flow rate was 10 l/hr, the effective furnace volume amounting to about 100 cm^3. The specimen was first suspended in the quartz part of the furnace, which was pulled out of the heated part. The whole apparatus was then flushed with argon for several hours and next flushed for about $\frac{1}{2}$ hr with the SO_2 gas mixture used for oxidation. The reaction was started by inserting the quartz part containing the specimen into the heated part of the furnace (800°C). The temperature in the reaction volume rose to this value within about 10 min. After the run was finished the whole apparatus was cooled in argon. The specimens were then sealed in methylmethacrylate, after which they were cut and examined by standard metallographic methods. Radioactive sulfur was located by means of autoradiographs using lithographic plates FO5 produced by VEB Filmfabrik, Wolfen, DDR.

RESULTS

Low SO_2 Partial Pressures (0.03 atm)

For partial pressures less than 0.2 atm the scale has a complex structure.[1,2,3] According to the authors of Refs. 1, 2, and 3, a very thin wüstite layer is formed at the metal–scale interface. This layer contains small irregular islets of FeS. Above it there is a region of scale consisting of thin FeO and FeS lamellae. Outside this region there is a mixture of magnetite and FeS grains. At the scale–gas interface an Fe_3O_4 layer free of the sulfide is formed.

On the basis of investigations carried out by means of the marker method it has been found in the present work that on the flat surface of the specimen where the contact between the scale and the metal core is the longest, the scale-growth process occurs by means of outward diffusion of iron ions, which is in agreement with the results of Flatley and Birks.[1] This is illustrated by the position of the marker, which after the reaction is located at the metal–scale interface (Fig. 2). The autoradiograph of the specimen subjected to double-stage oxidation indicates also the existence of a small contribution of inward sulfur transport. Figure 3 shows the autoradiographs of a section of an iron specimen oxidized for 3 hr in nonradioactive SO_2 and

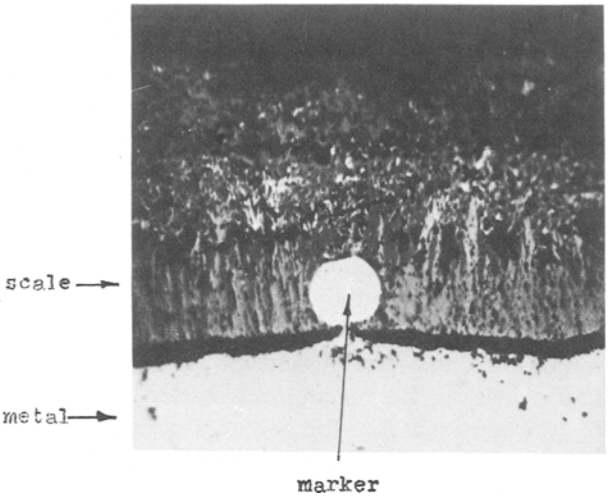

Fig. 2. Photomicrograph of a fragment of the section of an iron specimen oxidized for 4 hr in an argon + 3% SO_2 mixture at 800°C. Flow rate 10 l/hr.[8] ×200; reduced 30% for reproduction.

for 1 hr in radioactive SO_2. Dark parts indicate the presence of radioactive sulfur. It is seen that the sulfur radioisotope introduced in the second stage of the reaction is present not only in the outer part of the scale but also in the thin layer adhering directly to the metal.

In agreement with Ref. 1 it has also been found that at a certain thickness of the scale there occurs a separation from the metal core, first at the edges and finally at the flat surfaces.

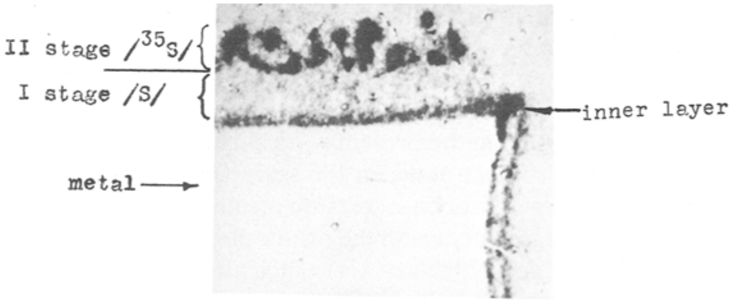

Fig. 3. Autoradiograph of an iron specimen oxidized in two stages (3 hr in nonradioactive SO_2 and 1 hr in $^{35}SO_2$) in a mixture of argon and 3% sulfur dioxide. Temperature 800°C, gas flow rate 10 l/hr.[8]

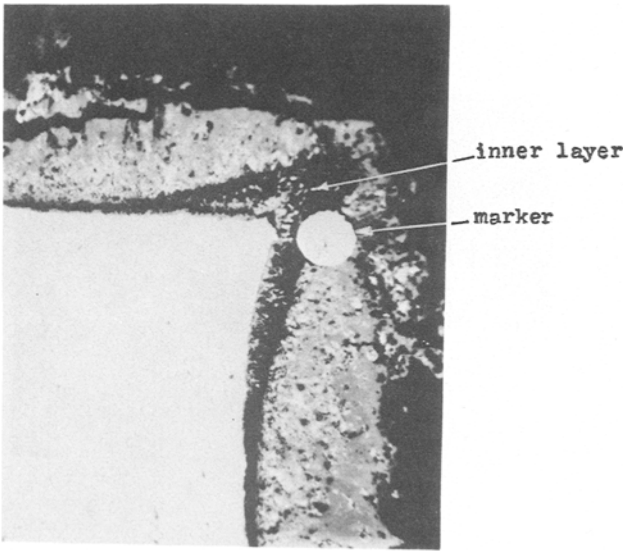

Fig. 4. Photomicrograph of a section of the edge of the iron specimen shown in Fig. 2.[8] ×200; reduced 30% for reproduction.

The marker method has made it possible to establish the fact that when contact between the metal and the scale is lost an inner layer is formed. Figure 4 shows a photomicrograph of a section of the specimen edge (the same specimen as in Fig. 2) with a visible marker. The position of the marker above the layer formed at the place where the scale is disconnected from the metallic core indicates that this layer was formed at the metal–scale interface. In the flat part of the specimen where the scale–metal contact was better, the marker remained at the metal–scale interface (Fig. 2). According to Flatley and Birks,[1] when the contact between the scale and the metal substrate is lost, the sulfide dissociates at the metal–scale interface. The iron ions produced then migrate to the scale surface where they react with the gas, thus building up the outer layer. On the other hand, sulfur from this dissociation reacts with the surface of the metallic substrate. Such a mechanism has been proposed earlier by Mrowec and Rickert[5] and by Brückman *et al.*[6] in the case of pure-metal sulfidation.

Radioisotope studies performed by means of the two-stage oxidation method have shown the presence of radioactive sulfur in the layer formed under the marker at the edge of the specimen. This is illustrated in Fig. 3 where a black outline of this layer is seen at the edge of the specimen. Figure 5 shows a photomicrograph of the section of the edge of the same specimen.

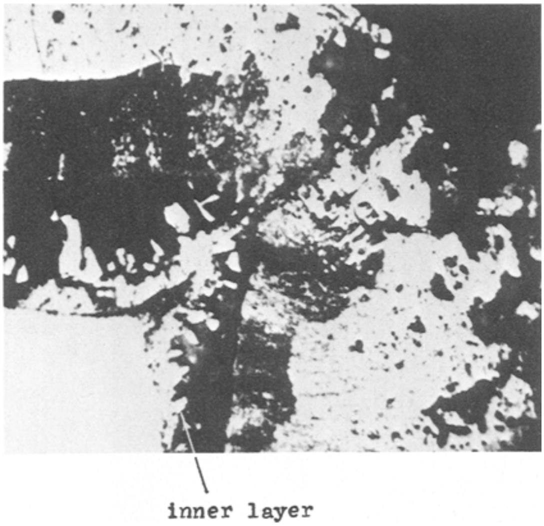

Fig. 5. Photomicrograph of the section of the specimen edge whose autoradiograph is shown in Fig. 3.[8] ×200; reduced 30% for reproduction.

The above results indicate that the iron sulfide at the metal surface forms by utilizing some sulfur from the dissociation of the inner side of the scale, as well as some which penetrates from the outside. Such a mechanism can also explain the presence of radioactive sulfur at the flat surface of the metallic core (Fig. 3) where the contact between scale and metal has been lost also.

As mentioned before, Rahmel[4] and Flatley and Birks[1] give two possible mechanisms for inward sulfur transport: penetration through discontinuities in the scale (which is favored by its structure) in the form of SO_2 or elementary sulfur and diffusion, due to the solubility of sulfur in iron oxide.

On the autoradiographs of the iron specimen oxidized in two stages (Fig. 3) one can observe darker tracks in the nonradioactive part of the scale. These tracks probably show the paths of inward migration of sulfur. This indicates the existence of preferential paths of inward transport, e.g., through discontinuities in the scale or exchange between particular grains, rather than by volume diffusion.

SO_2 Pressure of 1 atm

According to Flatley and Birks,[1] the scale produced on iron at temperatures ranging from 600 to 900°C and SO_2 partial pressures from 0.2 to 1 atm

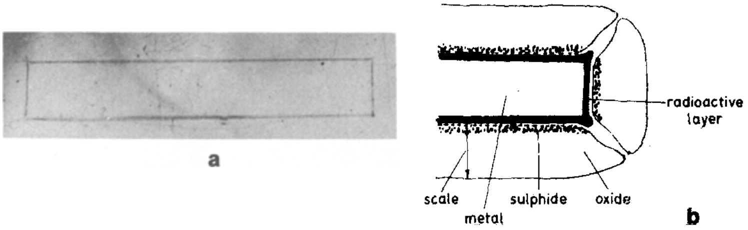

Fig. 6. Autoradiograph (a) and schematic drawing (b) of an iron specimen oxidized for 12 hr in SO_2 and 5 hr in $^{35}SO_2$ ($p_{SO_2} = 1$ atm).

is very similar to that produced in pure oxygen, except for a very thin layer at the metal–scale interface which contains iron sulfide. In the present paper it has been found by means of the marker method that if the contact between metal and scale is maintained the reaction occurs mainly by outward diffusion of iron ions similarly as for low SO_2 pressures. However, investigation by means of the two-stage oxidation method has shown the presence at the metal–scale interface of a small amount of radioactive sulfur introduced in the second stage. Figure 6 shows the autoradiograph of a specimen oxidized for 12 hr in nonradioactive SO_2 and then for 5 hr in $^{35}SO_2$. Dark spots indicate the presence of ^{35}S. This result indicates the existence of inward transport of sulfur to the metal–scale interface.

The autoradiograph of the specimen after 16 hr of oxidation in nonradioactive SO_2 and 2 hr in $^{35}SO_2$ is shown in Fig. 7. The radioisotope which has been introduced in the second stage is present only at the edges of the

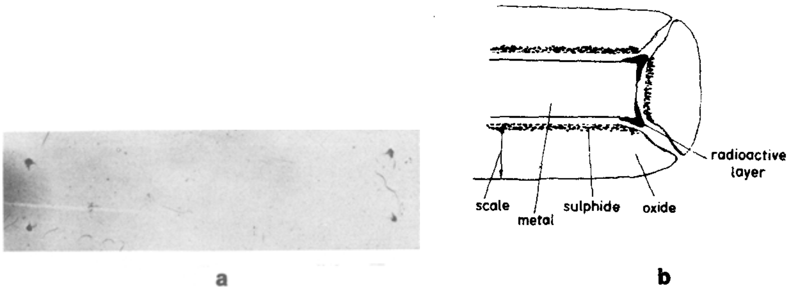

Fig. 7. Autoradiograph (a) and schematic drawing (b) of an iron specimen oxidized for 16 hr in SO_2 and 2 hr in $^{35}SO_2$ ($p_{SO_2} = 1$ atm).

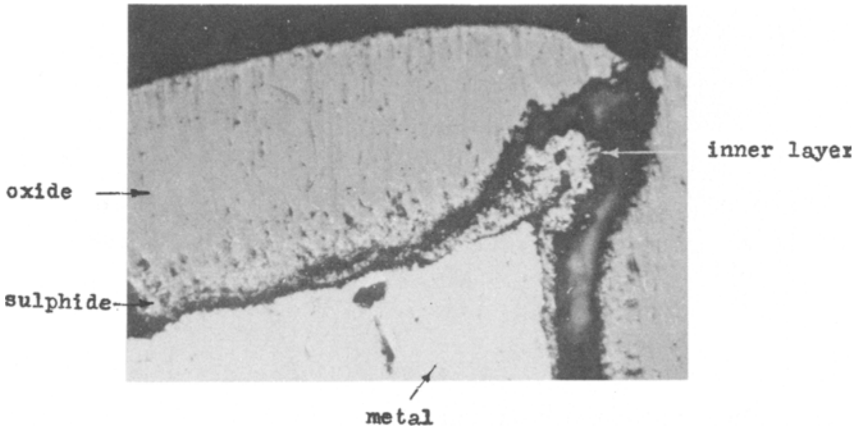

Fig. 8. Photomicrograph of a section of the edge of the specimen shown in Fig. 7. ×200; reduced 30% for reproduction.

specimen. Figure 8 shows a photomicrograph of a section of the edge of the same specimen. A fissure can be seen at the edge of the specimen which has probably been produced by dissociation of the scale from its internal side. An indication that this is really the case is given by the rounded edges of the fissure. If it were formed during the cooling process the boundaries of the crack would be approximately parallel. At the edge of the specimen one can see in Fig. 7 the internal layer in which the radioactive sulfur is deposited.

However, in the case of a specimen oxidized for 3 hr in nonradioactive SO_2 and next for 1 hr in radioactive SO_2 no radioactive sulfur was found in the scale. The reaction time was too short for the production of fissures from the metal surface to the outer scale surface.

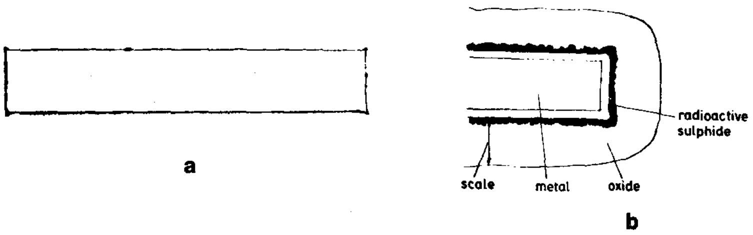

Fig. 9. Autoradiograph (a) and schematic drawing (b) of an iron specimen oxidized for 2 hr in $^{35}SO_2$ and 16 hr in SO_2. Temperature 800°C, flow rate 10 l/hr ($p_{SO_2} = 1$ atm).

In the autoradiographs in Figs. 6 and 7 no trace of inward penetration of radioactive sulfur has been found in the bright nonradioactive parts of the scales seen in the figures. The above-mentioned results indicate that at the specimen edges where the contact between the scale and the metal substrate is lost at the earliest stage dissociation of the scale occurs, resulting in the formation of fissures. Sulfur penetrates through these fissures from the outside atmosphere, either as S or in the form of SO_2. One should assume that the internal layer produced at the edges resulted from sulfur from both the dissociation of FeS in the scale and from the transport from the outside, as was the case for low SO_2 partial pressures.

Figure 9 shows an autoradiograph of a specimen which, in contrast to the former, was first oxidized for 2 hr in radioactive and then for 16 hr in nonradioactive SO_2. A thin dark FeS layer at the internal side of the scale is clearly seen. This whole layer contains radioactive sulfur, so it is evident that it has been produced in the first 2 hr of the reaction.

The above-mentioned experiment clearly shows that until fissures are formed, the sulfide found in that part of the scale which joins to the metal core is produced in the initial stage of the reaction and that no inward transport of sulfur contributes to its formation.

CONCLUSIONS

1. As long as the contact between the scale and the metal substrate is maintained, the scale growth is due to the outward diffusion of metal ions. This applies to both partial pressures of SO_2.

2. In those parts of the specimen in which the contact between the scale and the core has been lost an internal layer is produced. The location of the platinum marker in the specimen oxidized at 0.03 atm SO_2 pressure indicates that this layer was formed at the metal–scale boundary.

3. The results of radioisotope studies indicate that for both pressures the internal layer is produced also by sulfur penetrating from the outside atmosphere and not only by that from the inner scale boundary, as found by Flatley and Birks[1] in the case of low SO_2 partial pressures.

4. No inward transport of sulfur throughout the whole volume of the scale has been found, which means that there is no detectable volume diffusion of sulfur. The inward transport of sulfur to the metal occurs only through preferred paths. In the case of low SO_2 partial pressures these are probably discontinuities in the scale produced by its dissociation.

On the other hand, for $p_{SO_2} = 1$ atm it has been found that after a long reaction time (~16 hr) fissures might be produced at the edges of the specimen (probably by dissociation) through which sulfur from the outside penetrates to the metal surface, where it reacts with the metal.

However, sulfur penetrating from the outside does not contribute to the production of the thin FeS layer which is formed at the boundary with the metal. This layer is formed at the initial stage of the reaction.

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